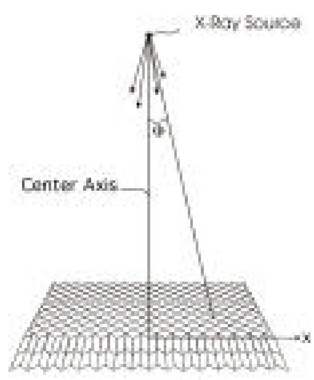
energy range from 3 keV – 30 keV. It will combine diffraction, x-ray fluorescence, and full-field imaging with absorption and phase contrast in a single instrument to study nanomaterials and nanostructures, with particular emphasis on the study of embedded structures. The nanoprobe, in its various operational modes, will allow real space mapping of (1) density and elemental composition through transmission, (2) crystallographic phase, strain, and texture through diffraction, (3) trace elements through fluorescence, (4) chemical states through spectroscopy, (5) magnetic domain structure through linear and circular dichroism, and (6) morphology through tomography. The nanoprobe will be a versatile tool that can be used, for example, to image and track domain evolution in ferroelectric and magnetic nanostructures, to observe strains in microelectronic interconnects, to measure composition and phase distributions in layered nanoparticles for catalysis, or to determine the position and chemical state of hybrid inorganic/organic nanoparticles interacting with biological systems.

1.9 High-Resolution X-ray Scattering

The High-Resolution X-ray Scattering (HRX) Group's activities are focused on developing x-ray optics and applications in nuclear resonant scattering, inelastic x-ray scattering**,** and other applications of high-resolution x-ray scattering techniques to fundamental measurements with resolution power exceeding 10^7 in the hard x-ray regime between 6-30 keV. The development emphasis is on mono-chromators, analyzers, detectors, software, and methodology.

Inelastic nuclear resonant scattering allows direct determination of partial phonon density of states in samples containing a suitable isotope with a low-energy nuclear transition with sub-meV energy resolution. **Coherent nuclear resonant scattering** allows determination of electronic and atomic structure around the probe atom through measurements of hyperfine interaction parameters in the neV energy scale. This is a particularly interesting area for nanoscale magnetism in thin films and multilayers, especially when combined with polarization-selective x-ray scattering techniques at nuclear resonance energy.



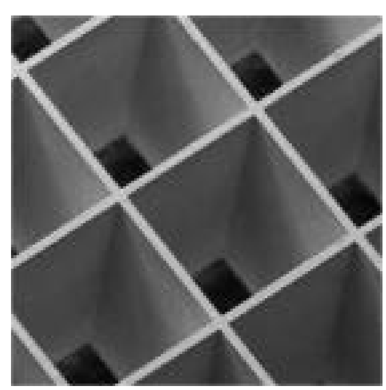


Fig. 1.29. Left: Ideal collimating grid with square septa oriented to a point x-ray source at 60 cm. Right: Copper septa are 25 μm thick and over 1,000 μm high (aspect ratio >40).

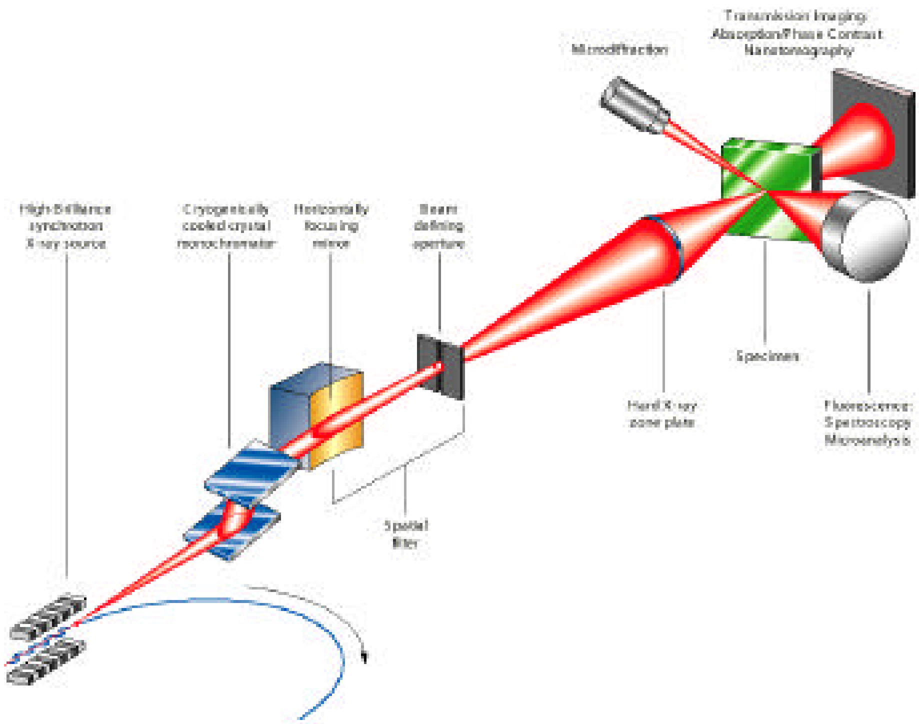


Fig. 1.30. Schematic of the scanning hard x-ray nanoprobe. Two collinear APS undulator A insertion devices provide a tunable, high-brilliance x-ray source. Fresnel zone-plate lenses serve as focusing and imaging optics with a spatial resolution of 30 nm. A spatial filter consisting of a focusing mirror and a beam-defining aperture provides spatially coherent illumination of the zone plates.

Inelastic x-ray scattering, on the other hand, enables measurement of phonon dispersion relations and form factors in single crystals, polycrystals, amorphous and liquid samples. The emphasis in nuclear resonant scattering is developing unique applications, like high pressure, biological materials, and thin films and multilayers. The emphasis in inelastic x-ray scattering is more on the spectrometer development, in terms of resolution, throughput, and accuracy.

Fundamental constant measurements are related to precision measurements of wavelengths and lattice constants with a precision exceeding current methods by two orders of magnitude. This may lead to establishment of new length standards at the Angstrom level and better definition of Avagdaro's constant. The applications are related to in-depth analysis of normal incidence diffraction (Sutter et al., 2001), x-ray Fabry-Perot interferometer (Sinn et al., submitted), use of LLL-interferometers for phase determination (Sturhahn, 2001), absolute wavelength measurements (Shvydko et al., 2000), and analysis of radiation from rotating frames (Röhlsberger et al., 2000; 2001) in the long pursuit of both µeV-resolved inelastic x-ray spectroscopy and measurement of lattice constant and thermal expansion coefficients of pure germanium isotopes (Hu et al., submitted).

The uniqueness of the HRX Group's effort comes from several sources: a) the ability to provide highly monochromatic and widely tunable crystal monochromators with resolution power exceeding 10^8 over a large energy range, b) having access to well-defined nuclear resonance energies with a resolution exceeding 10^{13}, and c) the infrastructure at the APS that enables development of bent crystal analyzers and monochromators.

1.9.1 Introduction

High-resolution nuclear resonant x-ray scattering (NRS) and momentum-resolved inelastic x-ray scattering (IXS) programs are designated as “strategic instruments,” indicating their long-term development schedule and innovative scientific nature. This group was charged to develop instrumentation beyond the state-of-the-art for the specific scientific purpose of inelastic and nuclear resonant scattering. The energy range was limited to 6 – 30 keV to cover a half dozen suitable nuclear resonant isotopes and appropriate backscattering energies of silicon crystals used for analyzers. These are shown in Table 1.2. An optimized undulator with a period of 2.7 cm was chosen to cover this range within the first and third harmonics.

When the beamline was planned in 1993-95, state-of-the-art high-resolution monochromators were 5 meV at 14 keV and 15 meV at 24 keV. Within the first five years, this has been pushed to sub-meV levels between 10-30 keV, with a record resolution of 1.7×10^8 at 24 keV, corresponding to 0.14 meV. Table 1.2 provides a comparison to highlight the progress at sector 3.

The current development in high-resolution monochromatization involves incorporation of more artificial channel-cut assemblies to allow new 4-crystal geometry to switch from (+ + - +) to (+ - - +), enabling 1-meV-level monochromatization at x-ray energies below 10 meV. Furthermore, feasibility tests are being performed to provide cryogenically cooled monochromators for increased throughput and additional energy stability for energies above 20 keV. Great progress has been made to provide efficient, high-resolution analyzers. All the necessary technology for dicing, gluing, and bending is now available in-house, and the consistent results obtained provide confidence for a future beamline. The IXS-CAT, currently under construction, derives most of its optics infrastructure from the developments that have taken place at sector 3.

For the IXS program, sector 3 staff had adopted a novel approach by employing “in-line” scanning monochromators and “dynamically bent” backscattering analyzers. This approach enabled the development of both NRS and IXS at the same beamline and provided the opportunity to explore newer applications of high-resolution x-ray scattering in the areas of x-ray metrology, x-ray interferometry, and exact backscattering. Furthermore, we have quickly adopted several key developments in other areas of x-ray optics. These include x-ray focusing using Kirkpatrick-Baez (K-B) mirrors and the use of a diamond phase plate for the production of circularly polarized light with switchable helicity.

At sector 3, development of every new instrument coincided with their scientific applications. Higher resolution micro-focused beams for high-pressure applications, high-resolution in-line monochromators for multilayer and thin films, a sub-meV monochromator for protein dynamics, high-resolution circularly polarized beams for spin structure determi-

Table 1.2. Progress made in high-resolution monochromatization since the commissioning of beamline 3-ID. The isotopes refer to stable Mössbauer nuclei, and Si reflections refer to exact backscattering planes used as an analyzer for the momentum-resolved IXS spectrometer. Only the highest resolution achieved at a given energy is listed.

Energy (keV)	ΔE (meV)	ΔE (meV)	Purpose
	1996	2001	
9.4	-	1	^{83}Kr -resonance
14.4	5	0.6	^{57}Fe - resonance
21.5	-	0.6	Si(18 6 0) back reflection and ^{151}Eu resonance
23.88	15	0.14	^{119}Sn resonance
25.5	-	0.5	Si(13 13 13) back reflection and ^{161}Dy resonance

nation in magnetic multilayers, an in-line IXS spectrometer for structure determination of levitated liquids at temperatures exceeding 2,500K. In some cases, the developments were requested by users: the monochromator for ^{83}Kr at 9.4 keV, or the 1 meV overall resolution IXS spectrometer for IXS-CAT. In many other cases, it was a classic case of "supply-induced demand," namely presenting the potential to the scientific community through talks, at conferences, workshops, university colloquia, papers, and private communications. Four PhD students (P. Abbamonte, J. Sutter, M. Hu, and A. Alatas) completed their thesis research entirely at sector 3, and currently three others are pursuing their degree at the APS as they permanently reside here. Many individual National Science Foundation (NSF), Department of Energy (DOE), and National Institute of Health (NIH) proposals were granted based on the capabilities of sector 3 spectrometers. This intense outreach effort resulted in galvanizing the scientific community to generate two successful large-scale proposals to DOE and NSF to build a new beamline, IXS-CAT, at the APS.

The scientific program at sector 3 can be summarized as follows:

1) **Nuclear resonant scattering**
2) **Momentum-resolved inelastic x-ray scattering**
3) **Fundamental measurements**
4) **Technical developments**

These programs are complemented by rigorous x-ray optics and instrumentation programs, as well as pursuit of new opportunities in applications of high-resolution x-ray scattering.

1.9.2 Nuclear Resonant Scattering

The HRX Group introduced this particular scientific application in 1995, and we have maintained our worldwide leadership in this field to this date. In this period, the technique has been applied to Kr, Fe, Eu, Sn and Dy isotopes in the areas of **geophysics** (high pressure), **biophysics** (protein dynamics, model porphyrins), **material science** (thin films, multilayers, order-disorder phase transformations, nanomaterials, magnetism), **condensed matter physics** (phase transitions in correlated electron systems and phonon-magnon coupling), and **chemistry** (Kr-intercalated clatrathes). We have organized international scientific workshops in 1997 at Argonne National Laboratory and in 2001 at ESRF. We are also scheduled to organize the next International Inelastic X-Ray Scattering Conference (IXS-2004).

High-Pressure Applications

The geophysics community has received this program very well worldwide, and we are now trying to expand its reach to the solid-state physics community as well. Along these lines, the observation of magnon-phonon coupling through a magnetic phase transition driven by high pressure in FeO (wustite) is a good example, as shown in Fig. 1.31 (Struzhkin et al., 2001).

The new direction we are pursuing is to extend high-pressure measurements of phonon density of states to high temperatures (exceeding 2000K). This will allow mimicking of the earth's mantle and inner core, and thus the thermodynamic properties of perovskites and spinels can be deduced.

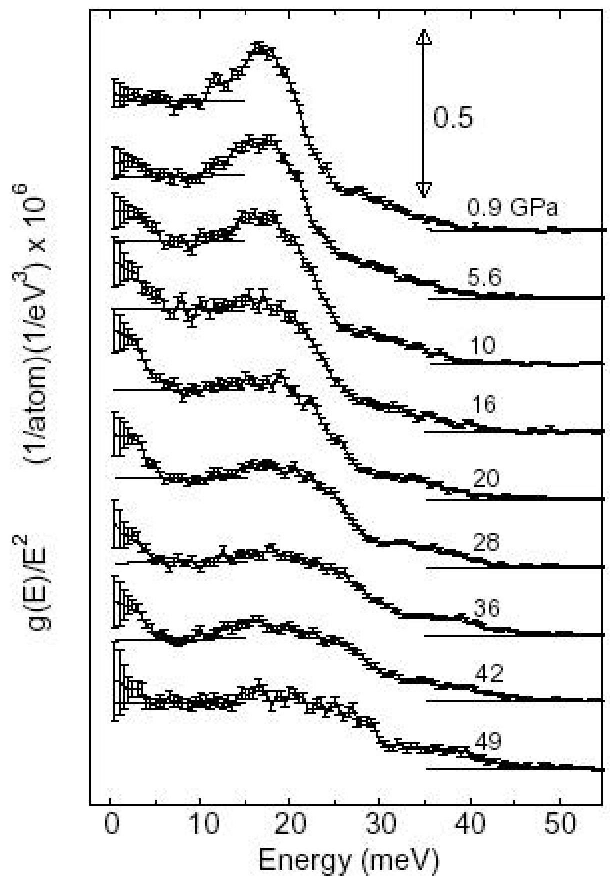


Fig. 1.31. The density of states of FeO, scaled with square of energy, as a function of pressure. The deviation from parallel lines in the low-energy region is most pronounced as FeO goes through a magnetic phase transition. This deviation from classical Debye behaviour is attributed to phonon-magnon coupling.

Biophysics Applications

The functional dynamics of proteins is an area that can be studied via vibrational modes of iron located at the center of heme molecules. Recent studies performed on myoglobin photolysis, in which CO molecules can be photolyzed with exposure to laser light, indicated the feasibility of measuring the change in the displacements of Fe with CO addition (Sage et al., 2001). In an attempt to quantitatively understand the vibrational density of states, these studies have been extended to model compounds, and single-crystal studies on these model compounds proved the potential to unambiguously differentiate between in-plane and out-of-plane vibrational modes. Figure 1.32 shows the analysis of vibrational modes in (nitrosyl) iron (II) tetra-phenylporphyrin (Rai et al., 2002).

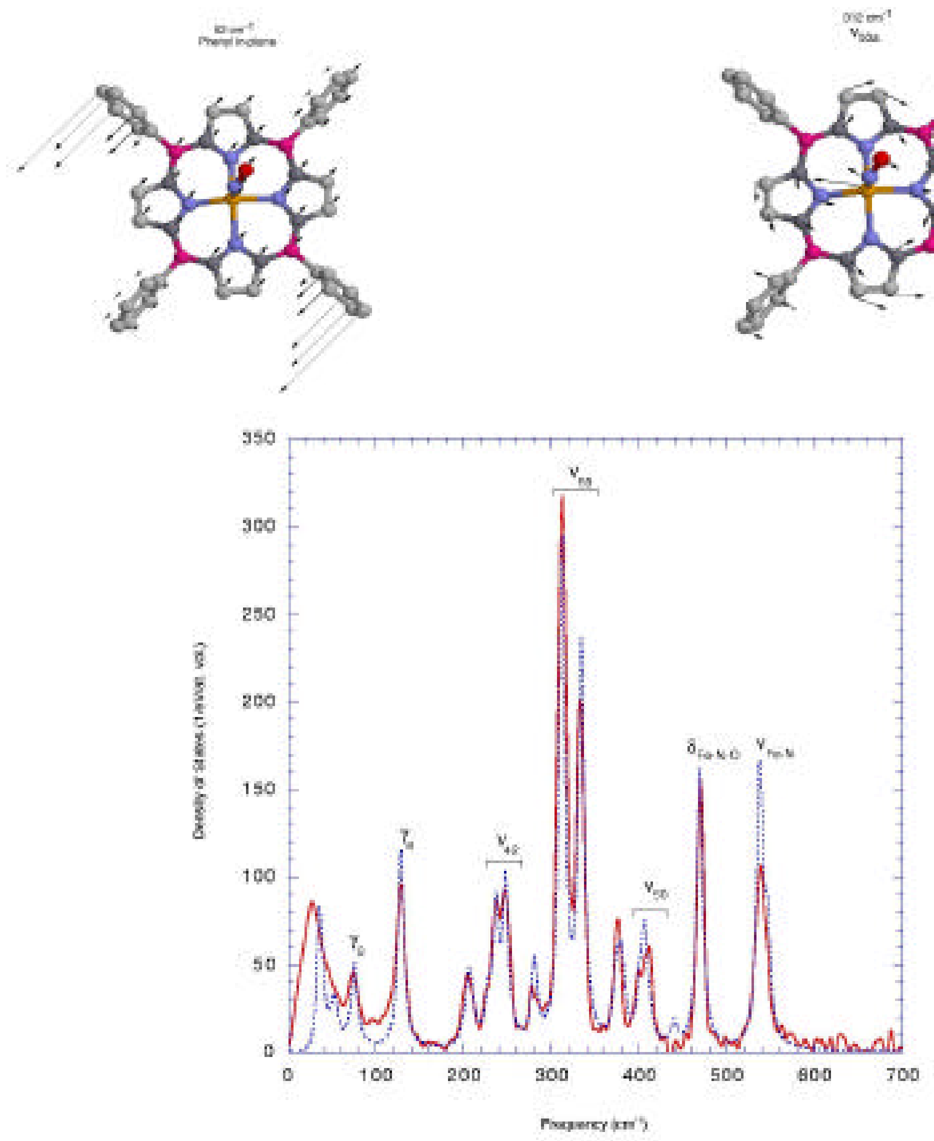


Fig. 1.32. Atomic displacements, their magnitude, direction and frequency measured through the iron atom in the center of the heme group.

Materials Science Applications

The measurement of vibrational properties from low-dimensional systems like thin films and multilayers has been extended to isotopically decorated layers, in which ^{57}Fe is selectively deposited at the interface or inside layers. Also, vibrational properties of amorphous layers in $Fe_{1-x}Tb_x$ and $Fe_{1-x}Y_x$ over a large composition range (18 < x < 80) have been studied. The emergence of soft phonon modes below 5 meV with increasing concentration of rare-earth element is interpreted as "boson peak," which needs to be understood in terms of a general explanation. Similar studies have been extended to Sn/Si multilayers (Roldan Cuenya et al., 2001), see Fig. 1.33.

1.9.3 Momentum-Resolved Inelastic X-ray Scattering

The inelastic spectrometer at the 3-ID-C station became available to outside users in 2000, and since then it has attracted a number of users from the materials physics and biology areas. Since this spectrometer is relatively new, a number of significant spectrometer improvements are still

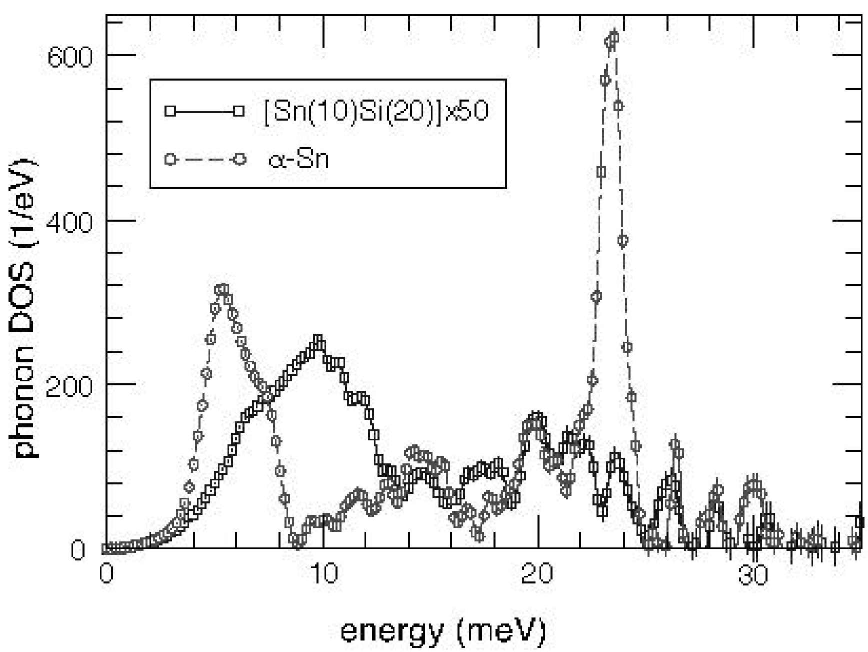


Fig. 1.33. The phonon density of states of α-Sn and a Sn/Si multilayer. The structure and vibrational dynamics of room-temperature-grown nanoscale Sn/amorphous (a)Si multilayers have been studied by ^{119}Sn nuclear-resonant inelastic x-ray scattering (NRIXS) of synchrotron radiation. With increasing Sn-layer thickness, the formation of β-Sn was observed, except at the Sn/Si interfaces, where a 10-Å-thick metastable pure amorphous a-Sn-like layer remains stabilized. By means of NRIXS, we have measured the Sn-projected vibrational density of states (VDOS) in these multilayers, in particular, at the interfaces and in 500-Å-thick epitaxial a-Sn films on InSb as a reference. Further, the Sn-specific Lamb-Mössbauer factor (f-factor), mean kinetic energy per atom, mean atomic force constant, and vibrational entropy per atom were obtained.

underway. These are incorporation of dynamically bent analyzers, increasing the number of analyzers from 1 to 4, and increasing the momentum transfer range from 3 to 5 $Å^{-1}$. In addition, changes are being implemented in the station to accommodate a containerless laser melting setup for high-temperature liquid studies (exceeding 2500K) and suitable sample mounting for single-crystal studies. Also, for development of the high-energy-resolution inelastic x-ray scattering (HERIX) spectrometer of IXS-CAT, a prototype 1 meV spectrometer has been tested, and an overall resolution of 1.04 meV has been obtained. This work will continue in the coming two years to build a high-throughput analyzer to be installed at the IXS-CAT HERIX spectrometer.

Microscopic Dynamics in Liquid Alumina

The properties of high-temperature oxide melts are of considerable geophysical interest, e.g., for modeling the earth's mantle, but are also important to a variety of technological problems like nuclear waste confinement. However, access to microscopic transport properties is often difficult to obtain with conventional techniques like ultrasound or viscosimetry because of the high temperatures and chemical reactivity of the oxide melts. Here we present data obtained with IXS on a liquid aluminum oxide sample levitated on a gas stream and heated by an infrared laser. The data set shows up to 6 nm^{-1} well-defined side peaks corresponding to a longitudinal phonon-like excitation in the liquid (Fig. 1.34). From the positions and the widths of these peaks, the high-frequency sound velocity and sound damping can be determined up to 2800°C (Sinn et al., in press), see Fig. 1.34.

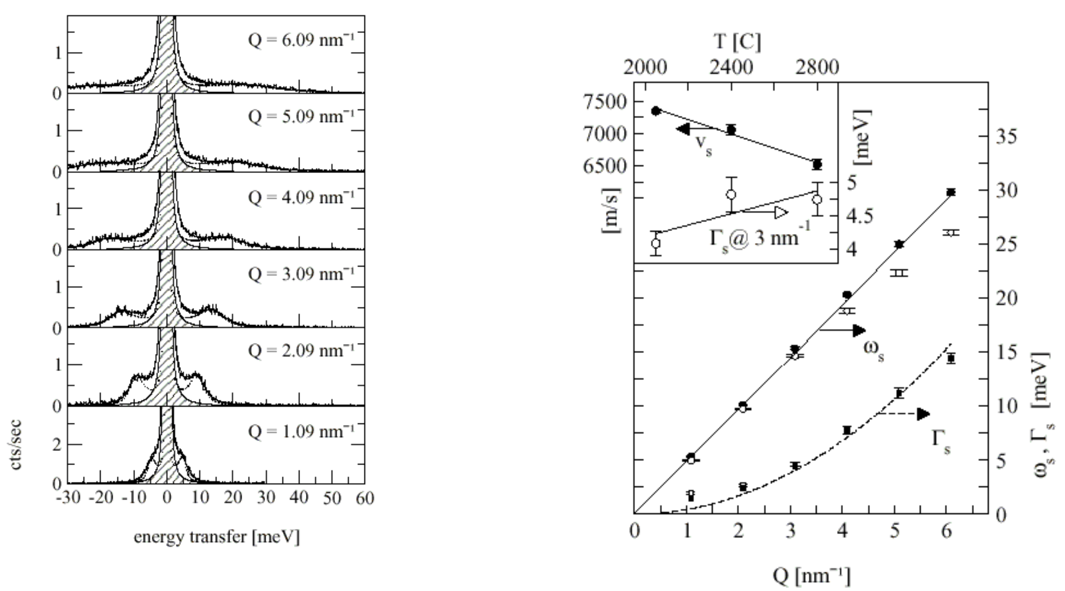


Fig. 1.34. Left: Inelastic x-ray spectra on liquid alumina at different momentum transfers. Right: Dispersion relation and damping obtained from the brillouin peaks. Inset: Temperature dependence of sound velocity and damping.

Liquid Mercury

Among the simple liquid metals, liquid mercury is the only one for which the critical point can be reached in a steady-state laboratory setup. In the vicinity of the critical point, the system undergoes a metal-to-nonmetal transition, which will affect the dynamics of the system dramatically towards a gas-like behavior with dimer formation. The persistence of these dimers in the liquid state has been the subject ofspeculation for some time. Due to the unfavorable cross section, mercury is difficult to investigate with neutrons. With x-rays, the most prominent problem is the high photoabsorption. In this measurement, we prepared a 20-µm-thick film between two sapphire crystals and measured in transmission geometry S(Q,ω) at different momentum transfers (see Fig. 1.35). Besides a quasi-elastic line, phonon-like excitations

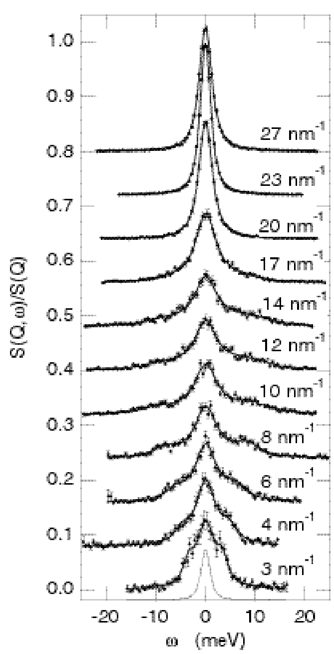


Fig. 1.35. Inelastic spectra of liquid mercury at different momentum transfers. The phonon-like excitations are visible as shoulders to the central peaks at small momentum transfers.

can be clearly resolved at low momentum transfers. For the data collected at room temperature, no indication of dimer formation could be found in the inelastic spectra (Hosokawa et al., in press).

1.9.4 Fundamental Constant Measurements and Interferometry

New applications for high-resolution x-ray scattering is a topic constantly pursued. The applications are related to in-depth analysis of normal incidence diffraction (Sutter et al., 2001), x-ray Fabry-Perot interferometer (submitted to Nature), use of LLL-interferometers for phase determination in nuclear forward scattering, and correct restoration of energy spectrum from the measured time spectrum (Sturhahn, 2001), absolute wavelength measurements (Shvydko et al., 2000), analysis of radiation from rotating frames (Röhlsberger et al., 2000; 2001), in the long pursuit of µeV-resolved inelastic x-ray spectroscopy, and measurement of lattice constant and thermal expansion coefficients of pure germanium isotopes (M. Hu et al., submitted) using normal incidence diffraction technique pioneered at 3-ID.

1.9.5 Technical Advances

The progress in scientific activities is directly coupled to the progress in technical capability developments. Along these lines, we can summarize the achievements in monochromators, analyzers, detectors, software development and methodology as follows.

Monochromators

The HRX group has been a recognized world leader in high-resolution monochromator development since 1992. Our emphasize is high-throughput, high-energy-resolution monochromatization for spectro-

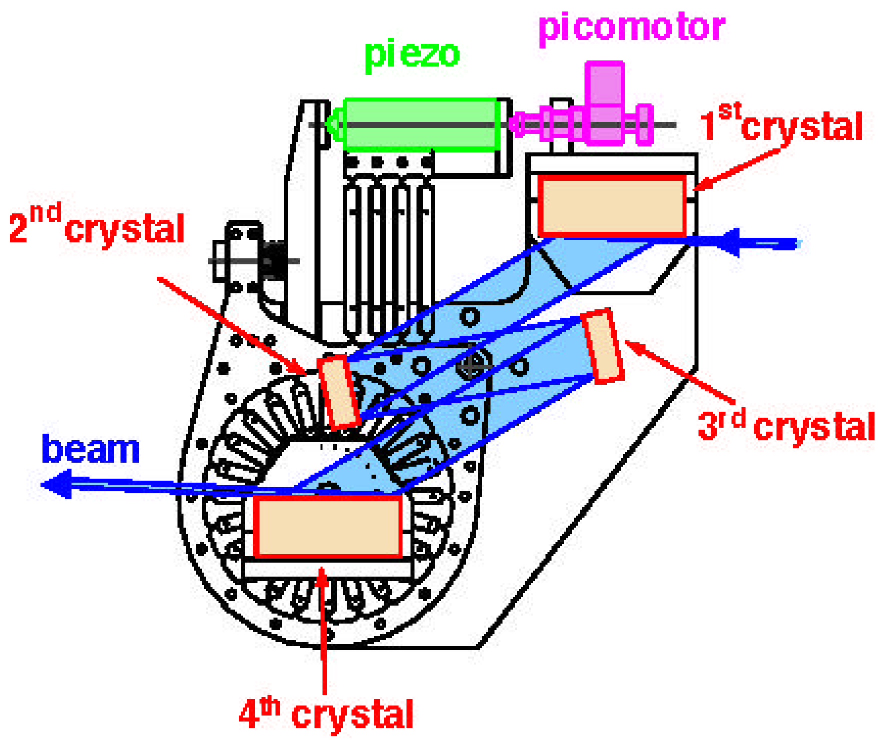


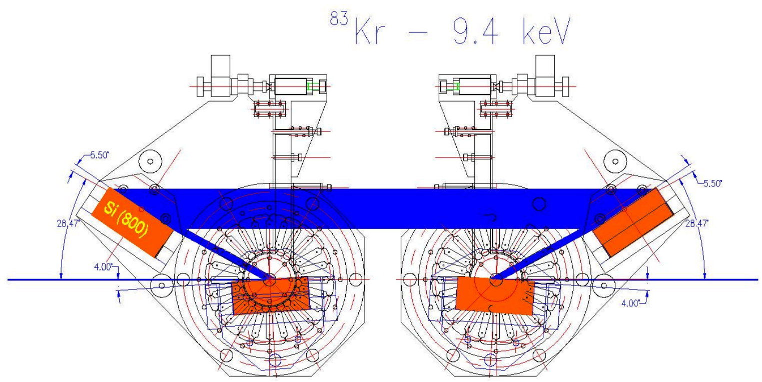
Fig. 1.36. A nested monochromator design, in which (++-+) geometry is used, and crystals 1 and 4 are linked the artificially, while crystals 2 and 3 were naturally channel cut. With this approach, it is possible to reach sub-meV above 20 keV, and, by cryogenic cooling, the throughput can be increased further. This is the current monochromator used for the 2 meV IXS spectrometer, 1 meV IXS spectrometer, 0.6 meV monochromator for ^{151}Eu, and 0.5 meV monochromator for ^{161}Dy nuclear resonance spectrometers.

scopy purposes. This program draws its strength entirely from the in-house talent and capabilities of XFD. In the last two years, the approach taken has been to exploit the artificial channel-cut technology (Shu et al., 2001) and optimization routines developed in crystal asymmetry and geometrical sequencing, for example, as shown in Figs. 1.36 and 1.37.

Analyzer Development

For momentum-resolved ineleastic x-ray spectroscopy, four highly efficient x-ray analyzers, which provide an energy resolution of about one meV, are essential. Typically, faceted silicon crystals in extreme backscattering geometry are used. To increase the efficience of these kind of ana1yzers, we developed a new way of cutting the silicon with a high-speed diamond saw. A piece of 4-mm-tick silicon is cut half way through with a relatively thick blade (300 μm) and then glued with the cut side to a flat glass wafer. Finally, the silicon is diced from the top with a fine blade (50 μm), leaving a substantial higher fraction of the area on top as compared to a one-way cut with a thicker blade that would be required for this cut depth (Fig. 1.38). The resulting "mushroom"-like structure is also favorable for stress release from the glued backside. The flat glass wafer is then bent by a two-dimensional bending device to the desired radius of about 6 m. With this new cutting technique and the more precise

(a)



(b)

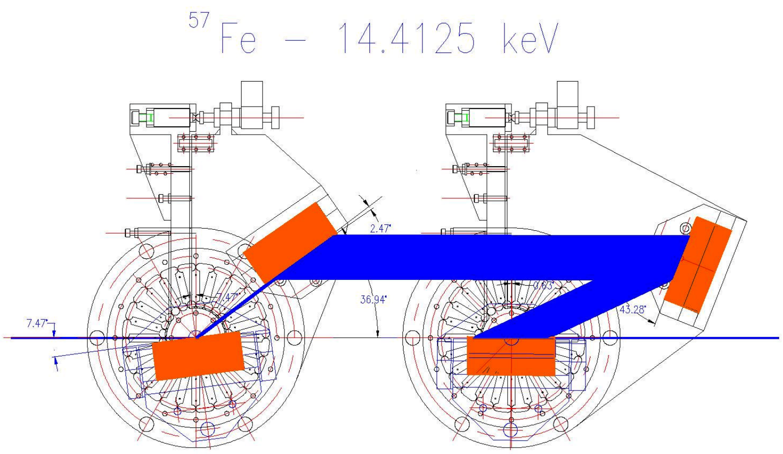


Fig. 1.37. The symmetric design of a new monochromator with (+-+-) geometry is used for (a) ^{83}Kr resonance at 9.4 keV, and (b) for ^{57}Fe at 14.4125 keV, both with a bandpass of 1 meV. The throughput is maximized by adjusting the asymmetry angles of the crystals, which are then linked with high-precision, high-stiffness links and thus called “artificial channel-cut.” Here, the first two crystals and the last two crystals are linked artificially, and the two assemblies are treated as two channel-cut crystals placed in dispersive geometry against each other. This monochromator is used in high-pressure ^{83}Kr lattice dynamics measurements and will be used for future ^{57}Fe isotope-based studies, since the exiting beam can be further focused using a Kirkpatrick-Baez type mirror.

bending, the efficiency of the analyzer was more than doubled (Sinn et al., in press).

Detectors

Nanosecond time-resolved detectors are at the core of the nuclear resonant scattering program. The HRX Group embraced the development of avalanche photodiode (APD) detectors very early. There is a need for high efficiency and large area detectors for different reasons. For example, for NRIXS measurements at ^{57}Fe, the 6.4 keV fluorescence photons can be best detected with thin APDs covering a large solid angle, while experiments with ^{119}Sn at 24 keV need highly efficient detectors. The HRX Group has been collaborating with Perkin-Elmer engineers to develop these type of detectors and also with engineers and scientists in Hamburg University for fast, low-noise, high-gain cascade pre-amplifiers. The fruits of these activities over the last two years will be available for users of the 3-ID beamline next year; these detectors (Figs. 1.39 and 1.40) are currently under commissioning at the beamline. We expect the overall data efficiency to improve by a factor of three once the detectors and the data acquisition system are integrated.

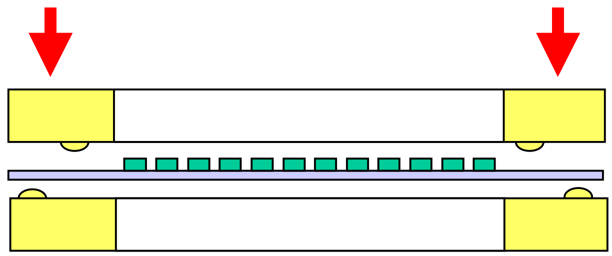


Fig. 1.38. Schematics of the analyzer bender (top). The newly developed two-sided cutting technique allows a larger reflecting area on the top at a given thickness of the silicon (bottom figures).

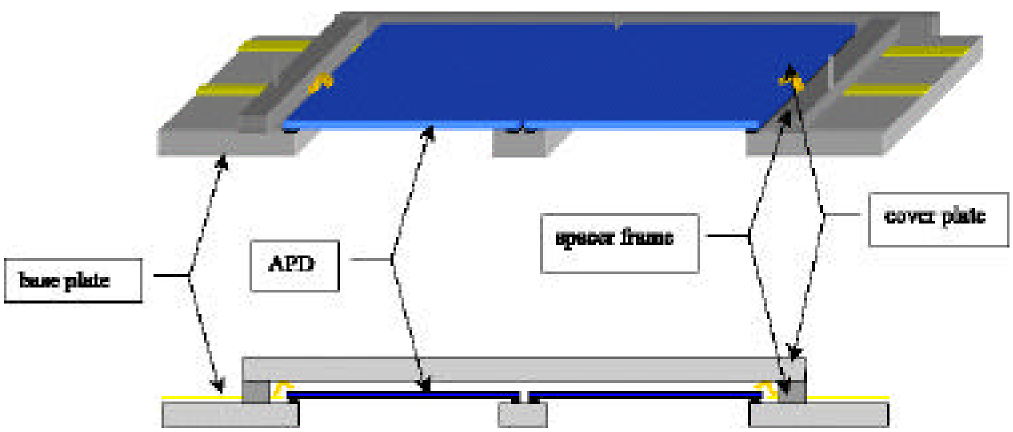


Fig. 1.39. A 4-element large-area detector, covering 20 x 20 mm, made from four independently activated square diodes, with 10 mm size.

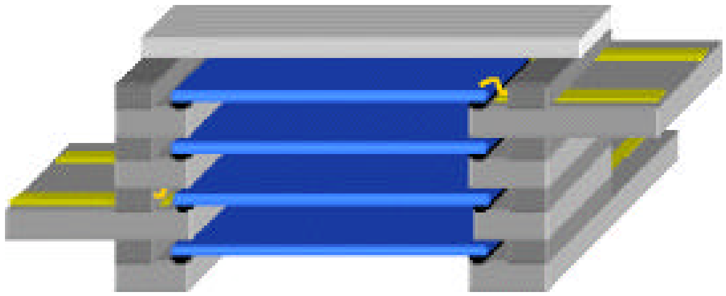


Fig. 1.40. A 4-element stacked-detector developed for high efficiency above 10 keV.

1.10 Polarization Studies

1.10.1 Introduction

The primary mission of the polarization studies program is to provide users with a high-brilliance, variably polarized x-ray beam. The polarized beams in sector 4 are produced by two separate undulators. To briefly review the main operational features, sector 4 has two branch lines, one for the "intermediate" (0.5 – 3 keV) and the other for the "hard" (> 3 keV) energy range. Variable polarization states are provided in the intermediate x-ray regime by a specialized circularly polarized undulator (CPU), while a planar undulator in combination with crystal optics has been used above 3 keV. A novel concept of spatially separating the beams from the insertion devices was successfully implemented for the first time at any synchrotron facility. The undulator axes are placed at a small angle (270 μrad) with respect to each other. A dipole electromagnet between the devices introduces the angular deviation of the electron beam, so 30 m away, in the first optics enclosure (FOE), the two beams are separated by 8 mm. This is sufficient to use two horizontally deflecting mirrors in the FOE to further separate the beams and deflect the intermediate energy x-ray beam down the beam pipe. This design enables simultaneous operation of both branch lines and thus more efficient utilization of the delivered beam. At the APS its success has been embraced in the design of several upcoming new beamlines (GM/CA-CAT, SER-CAT, SGX-CAT).

Since the last XFD Progress Report all the construction activities were completed. The beamlines were declared operational on July 15, 2001. Commissioning activities commenced with a vigorous schedule with the aim to achieve designed performance specifications by July 15, 2002. The bulk of the commissioning activities were directed towards the liquid-nitrogen-cooled double-crystal monochromator (DCM) and the torroidal mirror on the hard x-ray branch, and on the CPU and deflecting mirrors on the intermediate x-ray branch. By December 2001, the DCM operated according to theory, delivering 5×10^{13} photons/sec at 10 keV with Si (111) crystals. The torroidal mirror now focuses that flux to a spot size of 200 μm by120 μm in the horizontal and vertical directions, respectively. The CPU is currently commissioned to operate in the circularly polarized mode with a switching